DETERMINATION OF THE RATE CONSTANTS OF THE REACTION OF ATOMIC HYDROGEN WITH PROPANE AND n-BUTANE

N. I. Parsamyan and A. B. Nalbandyan

The reactions \( H + C_3H_8 \rightarrow H_2 + C_3H_7 \) (5a) and \( H + i-C_4H_{10} \rightarrow H_2 + C_4H_9 \) (5b) were studied in our earlier work [1] in the kinetic region of heterogeneous chain termination. The rate constants of these reactions, which proved equal to \( 0.8 \times 10^{-15} \exp(-8.4/RT) \, \text{(cm}^3\cdot\text{molecule}^{-1}\cdot\text{sec}^{-1}) \) (k5a) and \( 0.2 \times 10^{-15} \exp(-6.1/RT) \, \text{(cm}^3\cdot\text{molecule}^{-1}\cdot\text{sec}^{-1}) \) (k5b), were determined by the method of displacement of the first limit of ignition of hydrogen-oxygen mixtures in the presence of small quantities of the indicated hydrocarbons. However, as has already been noted [2], the data obtained in work in the kinetic region of destruction of active centers are not very accurate in view of the poor reproducibility of the experiments. For this reason, experiments on the determination of k5a and k5b were repeated under conditions under which chain termination occurs in the diffusion region, and therefore the reproducibility, at least in one series of experiments, is good. To bring about the destruction of active centers in the diffusion region, the surface of the reactor was treated with magnesium oxide [3, 4].

In the presence of small additions of hydrocarbon, the mechanism of combustion of a hydrogen-rich hydrogen-oxygen mixture at the first limit can be represented by the following sequence of elementary reactions [5-8]

\[
\begin{align*}
\text{(1)} & \quad \text{OH} + \text{H} \rightarrow \text{H}_2\text{O} + \text{H} \\
\text{(2)} & \quad \text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O} \\
\text{(3)} & \quad \text{O} + \text{H}_2 \rightarrow \text{OH} + \text{H} \\
\text{(4)} & \quad \text{H} \rightarrow \text{Surface} \rightarrow \text{Termination} \\
\text{(5)} & \quad \text{H} + \text{RH} \rightarrow \text{H}_2 + \text{R}
\end{align*}
\]

In this scheme, the reactions of atomic oxygen and OH radicals with RH were not taken into consideration. From an evaluation of the ratios of the rates of the corresponding reactions, it follows that for the composition of our working mixtures \( 4\text{H}_2 + \text{O}_2 \) (high concentration of hydrogen and very low concentration of RH) and the temperature interval in which we work (550-680\(^\circ\)), the rates of the reactions of O with RH and of OH with RH were approximately an order of magnitude below the rates of the reactions of O with \( \text{H}_2 \) and OH with \( \text{H}_2 \). As was indicated earlier [2], the destruction of O and OH on the wall under the conditions of our experiments can be neglected. As a result of reaction (5), the active H atom is replaced by the relatively inactive R radical, which then, reacting with oxygen, leads to the formation of the even less active HO\(_2\) radical and the corresponding olefin [5-11].

On the basis of the reaction scheme cited and the critical condition of ignition, the expression for the first limit can be represented in the following form:

\[
[\text{O}_2] = \frac{k_4}{2k_2} + \frac{k_5}{2k_2} [\text{RH}]
\]

where \( k_i \) are the rate constants of the corresponding reactions; \([\text{O}_2]\) and \([\text{RH}]\) are the concentrations of oxygen and the hydrocarbon at the limit. Equation (I) can be reduced to the form (IV)

\[
P_{p\text{O}_2} = \frac{k_4T^{2.5}}{2k_2} \cdot 0.97 \times 10^{15} + \frac{k_5}{2k_2} P_{p\text{RH}}
\]

where \( P_\text{O}_2 \), \( P_{p\text{O}_2} \) and \( P_{p\text{RH}} \) are the total pressure and partial pressures of oxygen and the hydrocarbon at the limit, respectively; \( k_4' \) is the portion of the constant \( k_4 \) that does not depend upon the temperature and pressure.

*The prime on the subscripts means that the reactions of heterogeneous chain termination took place in the kinetic region.

Fig. 1. First limits of ignition of mixtures of \(4H_2 + O_2\) (1) and \(4H_2 + O_2 + xC_3H_8\), where \(x\) (vol. %): 2) 0.100; 3) 0.198; 4) 0.296; 5) 0.400.

Fig. 2. First limits of ignition of mixtures of \(4H_2 + O_2\) (1) and \(4H_2 + O_2 + xn-C_4H_{10}\), where \(x\) (vol. %): 2) 0.050; 3) 0.148; 4) 0.182.

In a plot of \(P_{PO_2}\) versus \(P_{PRH}\), Eq. (IV) represents a straight line with a slope

\[ \text{tg} \alpha = k_\beta/2k_2 \]

and a segment intercepted on the Y-axis

\[ b = \frac{k_\beta^2}{2k_2 \cdot 0.97 \cdot 10^{19}} \]

The expression obtained by taking the logarithm of the quotient of the division of \(\text{tg} \alpha\) and \(b\) can be used to determine the rate constants of reactions (5a) and (5b):

\[ \log \frac{\text{tg} \alpha T^{2.5}}{b} = \log \frac{k_\beta}{k_\beta^2 \cdot 0.97 \cdot 10^{19}} - \frac{E_5}{2303RT} \]

In a plot of \(\log \frac{\text{tg} \alpha T^{2.5}}{b}\) versus \(\frac{1}{T}\), (VIII) is the equation of a straight line. From the slope of this straight line we can find the values sought for the activation energies \(E_{5a}\) or \(E_{5b}\), and from the segment intercepted on the Y-axis, we can find the pre-exponential factors of the constants \(k_{5a}\) and \(k_{5b}\).

Using the dependence of \(b\) upon the temperature, we can calculate the Arrhenius parameters of the rate constant of branching (2). Actually

\[ \log \frac{b}{T^{2.5}} = \log \frac{k_\beta}{2k_2 \cdot 0.97 \cdot 10^{19}} + \frac{E_2}{2303RT} \]

From the graph of this equation, it is not difficult to find \(E_2\) and \(k_\beta^1\). From (4) it follows that when \(PRH = 0\)

\[ b = \frac{k_\beta^2 T^{2.5}}{2k_2 \cdot 0.97 \cdot 10^{19}} = p_{H_2} p_{O_2}^{-1} \]

where \(p_{H_2}\) and \(p_{O_2}\) are the total pressure and partial pressure of oxygen at the limit for a mixture of \(H_2\) with \(O_2\) in the absence of the hydrocarbon. Consequently, at a given temperature, the segment intercepted by a straight line in a plot of \(P_{PO_2}\) versus \(P_{PRH}\) should be numerically equal to the product \(p_{H_2} p_{O_2}^{-1}\).

Figures 1 and 2 present the lower limits of mixtures of \(4H_2 + O_2\) with various additions of propane and n-butane, respectively. It is evident that an increase in the concentration of RH causes an increase in the limit, in accord with (I). The values of \(P_{PO_2}\) and \(P_{PRH}\) were calculated according to the data of Figs. 1.

*The crosses on the curves denote repeated measurements after the entire series of experiments to verify reproducibility.